BIODEGRADATION BEHAVIOR OF PALM OIL FIBER REINFORCED STARCH BIOCOMPOSITE

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ABSTRACT

The use of biodegradable materials from renewable resources had gained more attention in recent years. This research focus on the production of biocomposite from starch, glycerol and palm oil fiber whereby the fiber composition were 0%, 5%, 10%, 15% and 20%. The biocomposite produced was characterized in physical and chemical properties using Universal Testing Machine, Scanning Electron Microscope (SEM), Fourier Transform Infrared (FTIR), Differential Scanning Calorimetry (DSC), microbial degradation and soil burial degradation. This study revealed that the tensile strength increased by the addition of fiber until 10% but when the fiber compositions more than 10%, the tensile strength starts to decrease because of the poor adhesion between fiber and starch. On the thermal properties, the addition of fiber in the biocomposite improves the thermal stability as the melting point of the biocomposites increases when the fiber composition increased. For the biodegradability test, as the fiber composition increased, the longer time needed for the biocomposite to be degraded. Thus, the best performance of the biocomposites reinforced with fiber was at 10% fiber composition due to its higher mechanical testing and higher melting temperature. As a conclusion, the addition of fiber as a reinforcement in starch biocomposite can improve its mechanical strength, thermal properties and biodegradability whereby it had a various applications for biocomposites such as toys for children, furniture, flooring, and hardware for electronic products.

ABSTRAK

Penggunaan bahan biodegradasi dari sumber yang boleh diperbaharui telah mendapat lebih perhatian dalam beberapa tahun kebelakangan ini. Fokus kajian ini adalah menghasilkan biokomposit dari kanji, gliserol dan serat kelapa sawit di mana komposisi serat adalah 0%, 5%, 10%, 15% dan 20% dari serat kelapa sawit. Biokomposit yang terhasil dicirikan dalam sifat fizikal dan kimia dengan menggunakan mesin pengujian, mikroskopi pengimbasan elektron (SEM), spektroskopi inframerah transformasi Fourier (FTIR), kalorimeter pengimbasan perbezaan (DSC), biodegradasi menggunakan kaedah mikrobiologi dan kaedah timbus tanah. Kajian ini menunjukkan bahawa kekuatan ketegangan meningkat dengan penambahan serat sehingga 10% dari komposisi serat tetapi apabila komposisi serat melebihi 10%, kekuatan ketegangan menurun kerana percantuman yang lemah antara serat dan kanji. Bagi sifat haba, penambahan serat dalam biokomposit meningkatkan kestabilan haba dari biokomposit sebagaimana suhu degradasi dan takat lebur biokomposit meningkat apabila komposisi serat meningkat. Bagi ujian biodegradasi, apabila komposisi serat meningkat, masa yang diambil untuk biokomposit mendegradasi lebih lama. Dengan demikian, prestasi terbaik daripada biokomposit diperkuatkan dengan serat adalah pada komposisi serat 10% kerana ujian mekanikal dan takat lebur yang lebih tinggi. Sebagai kesimpulan, penambahan serat sebagai memperkuat biokomposit kanji dapat meningkatkan kekuatan mekanikal, sifat haba dan biodegradasi dimana ia mempunyai pelbagai aplikasi untuk biokomposit seperti mainan untuk kanak-kanak, perabot, lantai, dan peranti keras untuk produk elektronik.

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$℃$	-	Celcius
ΔH_c	-	Crystallization enthalpy
ΔH_m	-	Heat of fusion
AFM	-	Atomic Force Microscopy
DSC	-	Differential Scanning Calorimetry
EFB	-	Empty Fruit Bunch
FTIR	-	Fourier Transform Infrared
h	-	Hour
NaOH	-	Sodium hydroxide
MPa	-	Mega Pascal
SDA	-	Sabouraud Dextrose Agar
SEM	-	Scanning Electron Microscope
TA	-	Thermal Analyzer
TGA	-	Thermogravimetry Analysis
T_c	-	Crystallinity temperature
T_g	-	Glass transition temperature
T_m	-	Melting temperature
W_0	-	Original weight
W_2	-	Final weight
W_{loss} %	-	Final percentage loss in weight

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Biocomposite is a material formed by a matrix of starch and reinforced by natural fibers that usually derived from plants or cellulose. It has a wide-range uses such as for drug and gene delivery, tissue engineering applications and cosmetic orthodontics. They often mimic the structures of the living materials involved in the process in addition to strengthen the properties of the matrix that was used but still providing biocompatibility, for example in creating scaffolds in bone tissue engineering (Coats *et al*., 2008).

Natural fiber reinforced starch biocomposite have recently gained importance in various applications such as building materials and automotive components. The natural fibers offer advantages of large quantity, annual renewability, low cost, light weight, competitive specific mechanical properties, reduced energy consumption, and environmental friendliness. The natural fibers used to reinforce bio-plastics mainly include wood, cotton, flax, hemp, jute, sisal, and sugarcane fibers (Mohanty *et al*., 2000).

Natural fibers also can be a renewable and cheaper substitute for synthetic fibers, such as glass and carbon and have numerous advantages, such as low cost, low density, high toughness, acceptable specific strength properties, ease of separation and biodegradability. However, the main drawback of natural fiber may be their hydrophilic nature, which decreases the compatibility with hydrophobic polymeric matrix. In these composite fields, therefore, most of the research has

focused on improving interfacial properties between the polymer matrices and natural fillers in order to enhance the physical and mechanical properties of the end products (Lee *et al.*, 2009).

The current biodegradable polymers may be divided into synthetic and natural polymers, where the latter are classified into those of plant and microbial origin. The degradation of such polymers includes the disintegration into their monomers. Therefore unstable and hydrolysable linkages are required, where chemical, biological or photochemical reactions can take place. A huge number of biodegradable polymers have been synthesized chemically or by microorganisms and plants (Cañigueral *et al.*, 2009).

Among these, starch is a potentially useful material for biodegradable plastics because of its natural abundance and low cost. Starch is the major carbohydrate in plant tubes and seed endosperm, where it is found as granules. Each granule contains amylopectin molecules together with a larger number of smaller amylose molecules. The largest source of starch is corn and the other commonly used sources are wheat, potato and rice (Satyanarayana *et al*., 2008).

Awareness in using bio-plastics as a solution for environmental problems can help to lower down the burden caused by the plastics waste. Thus, less money will be allocated to the management of plastics waste and air pollution created from the burning of these non-degradable plastics.

In this research, we are fabricating biocomposite using starch and mix it with the natural fibers derived from palm oil fiber waste. Thus we can reduce the amount of pollution where we reuse waste produced from palm oil industries to create beneficial product such as biocomposite.

1.2 Problem Statement

Petrochemical based plastics such as polyolefin, polyesters and polyamides have been increasingly used as packaging materials because of their availability in large quantities at low cost and favorable functionality characteristics such as good tensile and tear strength, good barrier properties to oxygen and aroma compounds and heat seal ability (Goda *et al*., 2007). However, this will causing depletion source of petroleum. The majority of engineered plastic materials used today are made from synthetic polymers. The use of conventional petroleum-based polymer products creates many potential problems due to their non-renewable nature and ultimate disposal. As these conventional, the synthetic polymers are not easily degraded because of their high molecular mass and hydrophobic character, they may accumulate in the environment and represent a significant source of environmental pollution potentially harming wildlife (Silva *et al*, 2000). Moreover, plastic waste disposal becomes a huge eco-technological problem and one of the approaches to solve this problem is the development of bio-composites. Bio-composites are composites material composed of biodegradable matrix and biodegradable natural fiber as reinforcement (Ewa *et al*, 2007). The addition of fiber from any other sources can be added to increase the physical properties of bio-composites such as tensile strength and elongation to break. Thus, by applying waste material such as oil palm fruit fiber waste, a least expensive and more environmental friendly composite can be produced. Hence, oil palm fruit fiber waste is the one of the alternatives of fiber that can use in the fabrication of bio-composite as it is natural abundance waste and least expensive.

1.3 Objective of the Study

The main objectives of this research are to produce bio-composites reinforced by palm oil fiber from empty fruit bunch and study the characteristic of physical and chemical properties of the bio-composite produced.

1.4 Scope of the Study

In order to achieve the objective, there are few scopes of work that have been identified as follows:

i. Study the effect of different percentage compositions of fiber that are 0%, 5%, 10%, 15% and 20%.

ii. To investigate the characteristics of the biocomposite by using Fourier Transform Infrared Spectroscopy, Differential Scanning Calorimetry, Scanning Electron Microscopy and Universal Testing Machine.

iii. To determine the biodegradability behavior of biocomposite by microbial degradation using *Aspergillus niger* (*A. Niger*) and soil burial degradation test.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Fiber reinforced biocomposites have played a dominant role for a long time in a variety of applications for their high specific strength and modulus. Recently, there has been an increasing interest in the completely biodegradable composites reinforced with natural fibers (Mohanty *et al.*, 2000), because they are renewable, biodegradable and environmentally friendly, not withstanding their use in low-cost applications (Cao *et al.*, 2004). The advantages of natural fibers over traditional reinforcing materials have been due to their acceptable specific strength properties, low cost, low density, good thermal properties, enhanced energy recovery and biodegradability. Natural fibers such as jute, sisal, pineapple, abaca and coir (Gassan *et al.*, 1999) have been studied as a reinforcement and filler in composites.

Natural fiber-reinforced composites have attracted the attention of the research community mainly because they are turning out to be an alternative solution to the ever depleting petroleum sources (Goda *et al*., 2007). The production of 100% natural fiber based materials as substitute for petroleum-based products was not an economical solution. A more viable solution would be to combine petroleum and bio-based resources to develop a cost-effective product with diverse applications. The application of natural fiber-reinforced composites has been extended to almost all fields.

Natural fibers were mainly composed of cellulose, lignin and hemicelluloses. In general there was 1–35% lignin content in fibers depending

mainly on fiber type. Ramie, hemp and flax fibers have very low lignin content (usually under 3%), whereas wheat straw and wood fibers possess high lignin content (respectively higher than 10% and 20%) (Kunanopparat *et al.*, 2007).

Natural fibers were hydrophilic in nature as they were derived from lignocellulose, which contain strongly polarized hydroxyl groups. These fibers, therefore, were inherently incompatible with hydrophobic thermoplastics, such as polyolefins. The major limitations of using these fibers as reinforcements in such matrices include poor interfacial adhesion between polar-hydrophilic fiber and nonpolarhydrophobic matrix, and difficulties in mixing due to poor wetting of the fiber with the matrix. This in turn would lead to composites with weak interface (Alvarez *et al*., 2008).

Tserki *et al*. (2005) reported that there were many parameters which affect the performance of a natural fiber-reinforced composite. The degree and type of adhesion cannot be estimated quantitatively even though its importance was well recognized. Aspect ratio has a considerable effect on composite properties, hence it is important to conserve fiber length as much as possible during composite processing operations. Fiber aspect ratio must be in the range of 100–200 for optimum effectiveness. Fiber orientation has a significant effect on composite properties. During processing, the fibers tend to orient along the flow direction causing mechanical properties to vary in different directions.

Futhermore, optimization of interfacial adhesion between natural fibers and polymer matrices (thermoplastic and thermoset) has been the focus of a large amount of research conducted during the past two decades. This manuscript attempts to review the latest advancements in the field of chemical modification of natural fibers.

2.2 Starch

Starch or amylum was a polysaccharide carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. Starch is produced by all green plants as an energy store and was a major food source for humans. Pure starch was a white, tasteless and odorless powder that was insoluble in cold water or alcohol. It consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Depending on the plant, starch generally contains 20 to 25% amylose and 75 to 80% amylopectin. Glycogen, the glucose store of animals, was a more branched version of amylopectin. Starch can be used as a thickening, stiffening or gluing agent when dissolved in warm water, giving wheatpaste.

Starch molecules arrange themselves in the plant in semi-crystalline granules. Each plant species has a unique starch granular size: rice starch was relatively small (about 2μm), potato starch have larger granules (up to 100μm). Although in absolute mass only about one quarter of the starch granules in plants consist of amylose, there were about 150 times more amylose molecules than amylopectin molecules. Amylose was a much smaller molecule than amylopectin.

2.2.1 Tapioca Starch

Tapioca was a starch extracted from the root of the plant species Manihot esculenta. This species, native to the Amazon but now cultivated worldwide. Tapioca was a staple food in some regions and was used worldwide as a thickening agent, principally in foods. Tapioca was gluten free, and nearly protein free. The commercial form of tapioca most familiar to many people was pearl tapioca.

Commercially prepared tapioca has many uses. The powder was commonly used as a thickener for soups and other liquid foods, and was also used as a binder in pharmaceutical tablets and natural paints. The flour was used to make tender breads, cakes, cookies, and other delicacies. Flakes were used to thicken the filling of pies made with fruits having high water content.

2.3 Natural Fibers as Reinforcements in Biocomposite

2.3.1 Introduction

Fibers were a class of hair-like materials that were continuous filaments or were in discrete elongated pieces, similar to pieces of thread. They can be spun into filaments, thread, or rope. They can be used as a component of composite materials. They can also be matted into sheets to make products such as paper or felt. Fibers were includes of three types: natural fiber, cellulose fiber and synthetic fiber. Natural fibers were made from plant, animal and mineral sources. Natural fibers can be classified according to their origin. There were two types of fiber that were vegetable fibers and animal fibers.

Vegetable fibers were generally comprised mainly of cellulose include cotton, jute, flax, ramie, sisal and hemp. Cellulose fibers serve in the manufacture of paper and cloth. This fiber can be further categorized into the following:

i. Seed fiber: Fibers collected from seeds or seed cases. e.g. cotton and kapok.
ii. Leaf fiber: Fibers collected from leaves. e.g. sisal and agave.
iii. Bast fiber or skin fiber: Fibers were collected from the skin or bast surrounding the stem of their respective plant. These fibers have higher tensile strength than other fibers. Therefore, these fibers were used for durable yarn, fabric, packaging, and paper. Some examples were flax, jute, kenaf, industrial hemp, ramie, rattan, soybean fiber, and even vine fibers and banana fibers.
iv. Fruit fiber: Fibers were collected from the fruit of the plant. e.g. coconut fiber.
v. Stalk fiber: Fibers were actually the stalks of the plant. E.g. straws of wheat, rice, barley, and other crops including bamboo and grass. Tree wood was also such a fiber.

The most used vegetable fibers were cotton, flax and hemp, although sisal, jute, kenaf, bamboo and coconut were also widely used. Hemp fibers were mainly used for ropes and aerofoils because of their high suppleness and resistance

within an aggressive environment. Hemp fibers were, for example, currently used as a seal within the heating and sanitary industries. These were the type of fiber which is:

i. Animal fibers generally comprise proteins; examples include silk, wool, catgut, angora, mohair and alpaca.
ii. Animal hair (wool or hairs): Fiber or wool taken from animals or hairy mammals. e.g. sheep's wool, goat hair (cashmere, mohair), alpaca hair, horse hair, etc.
iii. Silk fiber: Fiber collected from dried saliva of bugs or insects during the preparation of cocoons.
iv. Avian fiber: Fibers from birds, e.g. feathers and feather fiber.

2.3.2 Palm Oil Fiber

Palm oil fiber was equivalent to coconut fiber at a competitive price. Palm oil fiber was non-hazardous biodegradable material extracted from palm oil's empty fruit bunch (EFB) through decortation process. The fibers were clean, non-carcinogenic, free from pesticides and soft parenchyma cells. Palm oil fiber was natural fiber extracted from palm oil vascular bundles in the empty fruit bunch. During the manufacturing process of palm oil fiber, EFB were shredded, separated, refined and dried. The manufacturing process does not involved chemical process or exposure. Hence the palm oil fiber was clean and non-toxic .Palm oil fiber was mainly used in the manufacturing of mattresses, sofa/car seat and etc.

Palm oil fibers were versatile and stable and can be processed into various dimensional grades to suit specific applications such as mattress cushion production, erosion control, soil stabilization/compaction, landscaping and horticulture, ceramic and brick manufacturing, thermoplastic filler, flat board manufacturing, paper production, acoustics control, livestock care, compost, fertilizer, animal feed, etc.

Figure 2.1: Palm oil fibers

2.4 Fiber Treatment and Modification

2.4.1 Alkali Treatment

Alkali treatment was a common method to clean and modify the fiber surface to lower surface tension and enhance interfacial adhesion between a natural fiber and a polymeric matrix (Liu *et al*, 2004). Natural fibers were light and renewable; they were low-cost and high-specific-strength resource. For those reasons, natural fiber composites have already been applied for fabricating some products such as furniture and architectural materials. Recently, they have gained widespread use in the automobile industry. In their application, synthetic resins, such as polypropylene and polyethylene, were commonly used as a matrix for natural fiber composites. However, those composites often display problems of fiber–matrix compatibility which results in decrease of mechanical properties. Therefore, in order to improve the interaction between fiber and matrix, surface treatments were necessary for modifying fibers' morphology. Treatments using alkaline solutions have been applied by several researches to improve mechanical properties and fiber–matrix adhesion of natural fiber reinforced plastics such as polypropylene/flax, epoxy/flax, and polyester/kenaf. During alkali treatment, the fibers' physical structure changes as a result of alkali were bleaching action which removes waxy materials and impurities. This action often leads to improvement of the interfacial bonding between fibers and matrix (Gomes *et al*., 2007).

2.5 Characterization

2.5.1 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM), Figure 2.2 was a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

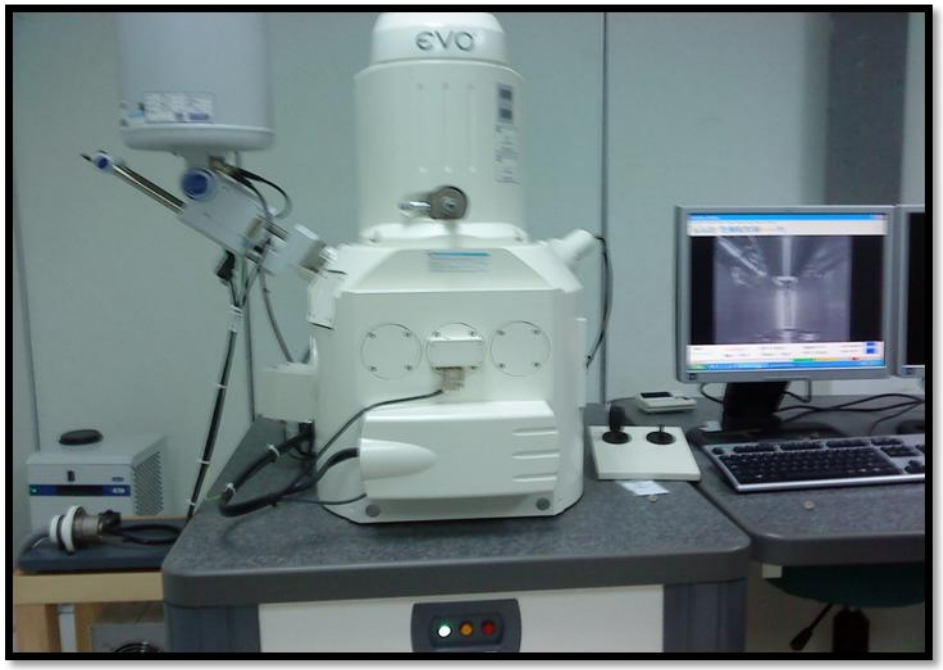

Figure 2.2: Scanning Electron Microscope

According to the previous study, Rosa *et al*. (2009) reported the effects of the different treatments on the surface fiber and the adhesion between fibers and matrix were investigated by SEM. From the microphotographs, fibers contain impurities, wax, fatty substances and globular protrusions called ‘‘tyloses”. The fiber surfaces were extremely heterogeneous, with smooth and rough portions in the same fiber. The role of the treatment was mainly to remove these impurities of the natural fiber, thus improving their wettability. Fiber washing was efficient in removing impurities. However, it did not remove the protrusions. Alkali treatment removed fatty-deposits and tyloses leading to the formation of a rough surface with pits, resulting in mechanical anchorage and reduced pullout and gaps between the fiber and matrix in

composite materials (Ma *et al*., 2005). Moreover, alkali treatment resulted in a higher amount of cellulose exposed on the fiber surface, thereby increasing the number of possible reaction sites.

Cañigueral *et al*. (2009) also suggests that the intrinsic tensile properties of fibers were proportional to fiber cross-sectional area associated with more perfect circle shape and regular form of the cross-sections. The shape of fiber cross-section was observed by SEM microphotographs.

2.5.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR stands for Fourier Transform InfraRed that showed in Figure 2.3 was the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation was passed through a sample. Some of the infrared radiation was absorbed by the sample and some of it was passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis:

i. It can identify unknown materials
ii. It can determine the quality or consistency of a sample
iii. It can determine the amount of components in a mixture

Alemdar *et al*. (2008) reported that FT-IR analysis of untreated and chemically treated fibers revealed the compositional changes in the fiber structures. The prominent peak at 1737 cm^{-1} in the untreated fiber was attributed to either the acetyl and uronic ester groups of the hemicelluloses or the ester linkage of carboxylic group of the ferulic acids of lignin or hemicelluloses. Moreover, the treatment of fiber with NaOH should reduce their hydrophilic behavior and polarity, resulting in a poor fiber matrix interface adhesion (Cañigueral *et al*., 2009). In addition, peaks at 3392 – 3425 cm^{-1} and around 1639.35 cm^{-1} were assigned to O-H stretching of hemicelluloses and C=O stretching of lignin in fiber and wave numbers at 1020 –

1052 cm^{-1} showed the presence of C-O bonds and this absorption peaks become more prominent as fiber loading increases (Aizan *et al*., 2008).

Figure 2.3: Fourier Transform Infrared (FTIR) Spectroscopy

2.5.3 Tensile Strength

Tensile strength was indicated by the maxima of a stress-strain curve and, in general, indicates when neckling will occur. As it was an intensive property, its value does not depend on the size of the test specimen. It was dependent on the preparation of the specimen and the temperature of the test environment and material.

A Universal Testing Machine, Figure 2.4 also known as a materials testing machine or materials test frame, was used to test the tensile stress and compressive stress of materials. It was named after the fact that it can perform many standard tensile and compression tests on materials, components, and structures.

Figure 2.4: Universal Testing Machine

According to Singh *et al*. (2007) reported that by embedding natural reinforcing fibers such as flax,hemp and ramie into a biopolymeric matrix made out of derivatives from cellulose, starch, polylactic acid, polycaprolactone for example, new fiber-reinforced materials called biocomposites have been created and were still currently being developed. Many studies have been carried out to investigate the suitability of natural fibers such as flax, jute, sisal, ramie, oil palm, cellulose as reinforcing components. Generally, the mechanical properties of the polymeric matrix were greatly improved.

Cañigueral *et al*. (2009) also reported that Young's modulus and tensile strength at break increase as fiber was added. Furthermore, the strain at break was reduced and seems to be stable as the fiber fraction increases, whatever the polymer matrix. Biocomposites have the same tensile behaviour as commonly used glass fiber composites. The maximal stress supported by the material increases and therefore, there was a transfer load mechanism from the polymer to the fiber. Furthermore, the strain at break seems to be constant and identical for all the composites. Consequently, one can conclude that the strain at break of the composites is dependent on the fibers (Bodros *et al*., 2007).

2.5.4 Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC), Figure 2.5 was a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference were maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The main application of DSC was in studying phase transitions, such as melting, glass transitions, or exothermic decompositions. These transitions involve energy changes or heat capacity changes that can be detected by DSC with great sensitivity.

Figure 2.5: Differential Scanning Calorimetry

According to previous study, Rosa *et al*. (2009) reported the thermal behavior of composites reinforced with treated fibers shows that the changes occurring in the fibers due to the treatments led to a positive effect on the thermal degradation behavior of the composites, as indicated by the higher thermal stability of the treated composites. Lovino *et al*. (2008) found that the starch exhibits glass transition T_g at